

RATIO OF THE Al^+ AND Hg^+ OPTICAL CLOCK FREQUENCIES TO 17 DECIMAL PLACES

W. M. ITANO,* T. ROSEN BAND, D. B. HUME, P. O. SCHMIDT,[†] C. W. CHOU,
 A. BRUSCH,[‡] L. LORINI,[§] W. H. OSKAY,[¶] R. E. DRULLINGER, S. BICKMAN,
 T. M. FORTIER, J. E. STALNAKER,^{||} S. A. DIDDAMS, W. C. SWANN, N. R. NEWBURY,
 D. J. WINELAND, AND J. C. BERGQUIST

National Institute of Standards and Technology, 325 Broadway, Boulder CO 80305, USA

**E-mail: itano@boulder.nist.gov*

Frequency standards (atomic clocks) based on narrow optical transitions in $^{27}\text{Al}^+$ and $^{199}\text{Hg}^+$ have been developed over the past several years at NIST. Both types of standards are based on single ions confined in Paul traps, but differ in the methods used to prepare and detect the internal atomic states. Al^+ lacks a strong, laser-accessible transition for laser-cooling and for state preparation and detection. Coupling with a Be^+ ion, trapped simultaneously with the Al^+ ion, enables state manipulation, detection, and cooling of the Al^+ ion. Both standards have achieved absolute reproducibilities of a few parts in 10^{17} . Development of femtosecond laser frequency combs makes it possible to directly compare optical frequencies. The present determination of $f_{\text{Al}}/f_{\text{Hg}}$ is 1.052 871 833 148 990 438 (55), where the uncertainty is expressed in units of the least significant digit. Measurements of $f_{\text{Al}}/f_{\text{Hg}}$ made over about one year show a drift rate consistent with zero. This result can be used to place limits on time variations of fundamental constants such as the fine structure constant α .

Keywords: atomic clocks, fundamental constants, optical frequency standards.

1. Introduction

Time, or its inverse, frequency, is the physical quantity that can be measured the most accurately and reproducibly. Bohr frequencies ν_{ij} corresponding to differences between two atomic energy eigenvalues E_i and E_j according to $\nu_{ij} = (E_i - E_j)/h$, where h is the Planck constant, are the basis for the most reproducible frequency standards. As opposed to frequency standards based on astronomical cycles or on vibrations of macroscopic objects, such atomic frequency standards have the advantage that the frequency-

determining objects, e.g., atoms of a particular type, are perfectly identical, so that two atomic frequency standards of the same type should have the same frequency.

In practice, frequency standards based on the same atomic resonance frequency do not agree exactly because of errors introduced for example by motion (Doppler shifts), by external fields that shift the frequencies, or by errors in the apparatuses used to determine the frequencies. The reproducibilities of atomic frequency standards have steadily improved. In 1967, the 13th Conférence Générale des Poids et Mesures redefined the SI (Système International) unit of time, previously based on astronomical motions, in terms of an atomic transition frequency.¹ Specifically, the SI second was defined as 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of ^{133}Cs . At that time, frequency standards

[†]Present address: Institut für Experimentalphysik, Universität Innsbruck, Austria.

[‡]Present address: Niels Bohr Institute, University of Copenhagen, Denmark.

[§]Present address: Istituto Nazionale di Ricerca Metrologica (INRIM), Torino, Italy.

[¶]Present address: Stanford Research Systems, Sunnyvale, CA 94089, USA.

^{||}Present address: Department of Physics and Astronomy, Oberlin College, Oberlin, OH 44074, USA.

based on cesium were accurate to about one part in 10^{12} . Currently the accuracy of cesium standards is about 3.3 parts in 10^{16} .²

There is nothing in principle to prevent an atomic frequency standard from being more reproducible than the best cesium standards. However, it is impossible to express a frequency in SI units (Hz) any better than the accuracy of cesium standards, since they define the SI unit of time. This limit does not apply to the measurement of a frequency *ratio* between two different frequency standards.

Frequency standards based on optical transitions in the mercury ion and, more recently, the aluminum ion have been developed at the National Institute of Standards and Technology (NIST). Both are based on narrow optical transitions in single trapped ions. According to estimates of their systematic uncertainties, both the mercury and aluminum standards are more reproducible than the primary cesium frequency standards. By means of a relatively new device, the self-referenced femtosecond laser frequency comb,³⁻⁵ the ratio of their frequencies can be measured without being limited by the accuracy of the cesium frequency standards. Measurements of this ratio as a function of time place limits on the variation of the fundamental constants, such as the fine-structure constant α .

2. Optical Frequency Measurements

2.1. Narrow Optical Sources

A prerequisite for a high-quality optical atomic frequency standard is a light source with extremely narrow linewidth and high frequency stability that can be tuned into resonance with the atomic transition. Lasers are now available with linewidths much less than 1 Hz.⁶ These lasers are frequency-stabilized in the short-term to optical resonators based on mirrors with extremely high

reflectivity. Since the mode frequencies of the resonator depend on its physical dimensions, they drift with time.

2.2. Optical Frequency Standards and Clocks

In an optical atomic frequency standard, the average frequency of a highly frequency-stable optical source is servo-locked to an atomic resonance frequency. In most cases this is done by stepping the frequency of the optical source slightly above and then slightly below the atomic resonance and detecting the difference in the probability of making a transition between the atomic levels. The apparatus uses this difference in signals to keep the average frequency of the optical source close to that of the atomic resonance.

An atomic frequency standard is not automatically usable as an atomic clock. Some means of counting the oscillations of the servo-locked electromagnetic field is required. With frequency standards based on atomic transitions at microwave frequencies, this is relatively straightforward, by use of conventional frequency multiplication, division, and mixing techniques.

Until relatively recently, the counting of optical frequencies was difficult, involving complex chains of frequency-doubled and frequency-mixed lasers. Now, with the self-referenced femtosecond laser frequency comb, the linkage of optical to microwave frequencies, required for the generation of time from a stable optical frequency, is relatively simple.

2.3. The Femtosecond Laser Frequency Comb

A self-referenced femtosecond laser frequency comb generates a series of discrete, equally frequency-spaced modes, called a "comb." The mode spacing, f_{rep} , is given by the repetition rate of a mode-locked laser, typically

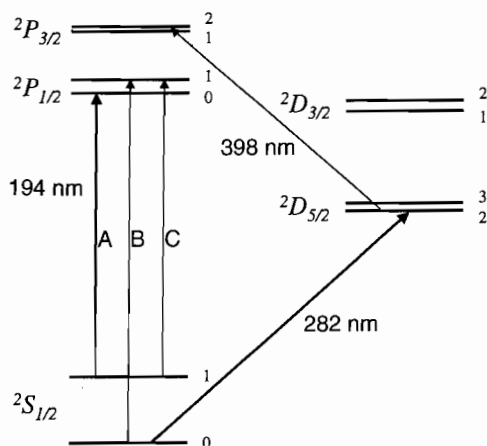


Fig. 1. The energy levels of $^{199}\text{Hg}^+$ relevant to the operation of the frequency standard. The numbers to the right of the hyperfine energy levels are F , the total atomic angular momentum. The transitions induced by the lasers are indicated by arrows. For clarity, the energy differences between the hyperfine levels are expanded relative to the electronic energy differences.

around 100 MHz to 1 GHz. The frequency of an individual mode can be expressed as $f(m) = f_0 + m \times f_{\text{rep}}$, where m is an integer. The repetition frequency is measured by directing some of the comb light to a photodetector. The offset frequency f_0 is measured by a method called self-referencing.^{4,5} If the heterodyne beat frequency f_{beat} between an optical frequency standard and the nearest tooth of the optical comb is measured, then the frequency of the standard is known in terms of f_0 , f_{rep} , and f_{beat} , provided the integer m is known. This provides a link between the optical frequency and the frequencies, f_0 , f_{rep} , and f_{beat} , which can be referenced to a microwave frequency standard.

3. The Mercury Ion Frequency Standard

3.1. Atomic Level Structure

The mercury ion frequency standard is based on the transition from the ground $5d^{10}6s \ 2S_{1/2}$ state to the metastable $5d^96s^2 \ 2D_{5/2}$ state. The metastable state

has a natural lifetime of around 90 ms, giving this transition a Q of around 6×10^{14} . Doppler broadening is eliminated for single-photon absorption by confinement of the ion to less than the wavelength of the radiation.⁷ Line broadening due to the magnetic field fluctuations is reduced by using the ($F = 0$) to ($F = 2, m_F = 0$) hyperfine-Zeeman component in $^{199}\text{Hg}^+$, which has only a quadratic Zeeman shift. The 282 nm resonance has been observed with a linewidth as low as 6.7 Hz.⁸

3.2. Operation of the Frequency Standard

The basic methods used for laser cooling, state preparation, and detection of the clock transition have been described previously.^{8,9} The energy levels of $^{199}\text{Hg}^+$ that are relevant to the operation of the frequency standard are shown in Fig. 1. The 194 nm $5d^{10}6s \ 2S_{1/2}$ to $5d^{10}6p \ 2P_{1/2}$ transition is used for Doppler laser cooling and laser-induced-fluorescence detection. The laser cooling and detection beam is tuned to component A in Fig. 1. To prevent trapping in a nonabsorbing dark state, the laser cooling and detection laser is polarization-modulated.¹⁰ A laser beam tuned to the B component prevents trapping in the ($F = 0$) ground state. To determine whether the 282 nm clock transition has been driven, radiation at the A and B frequencies is applied. If 194 nm fluorescence is observed, then the transition out of the ($F = 0$) ground state did *not* occur. A laser tuned to the 398 nm transition empties the $2D_{5/2}$ state. Prior to driving the 282 nm clock transition, the ion is prepared in the $2S_{1/2}$ ($F = 0$) hyperfine state by introducing a laser tuned to the C component to drive the ion from the $2S_{1/2}$ ($F = 1$) state to the $2S_{1/2}$ ($F = 0$) state.

With the frequency of the laser servo-locked to the atomic resonance, the apparatus functions as a frequency standard. With the aid of a self-referenced femtosec-

ond laser frequency comb, the frequency of the Hg^+ -stabilized laser has been compared to microwave or other optical frequency standards.^{11–17}

3.3. Limitations and Current Performance

The various contributions to the systematic uncertainty of the mercury ion frequency have been evaluated or estimated.^{14,17} The second-order Doppler shift due to thermal motion is reduced by laser cooling to near the Doppler cooling limit. The second-order Doppler shift due to rf micromotion is minimized by compensation of the stray electric fields.¹⁸ The static magnetic field is periodically measured by observing the resonance line of a first-order magnetic-field dependent Zeeman component of the $^2S_{1/2}(F=0)$ to $^2D_{5/2}(F=2)$ line. The frequency shift due to the interaction of the atomic quadrupole moment with a static electric field gradient is canceled by switching the magnetic field direction between three mutually perpendicular directions.^{14,19} The blackbody radiation shift is negligible because the trap is operated at liquid helium temperature. An AC Zeeman shift due to unbalanced rf currents in the trap electrodes has been estimated and found to be small.¹⁷

It has been estimated that none of these individual sources of uncertainty is greater, fractionally, than 1×10^{-17} . The total fractional systematic uncertainty, given by the quadrature sum of the individual terms, is 1.9×10^{-17} .¹⁷

4. The Aluminum Ion Frequency Standard

4.1. Atomic Level Structure

The energy levels of $^{27}\text{Al}^+$ relevant to the operation of the frequency standard are shown in Fig. 2. The lifetime of the 3P_0 state has been measured to be 20.6 ± 1.4 s,²⁰ so the

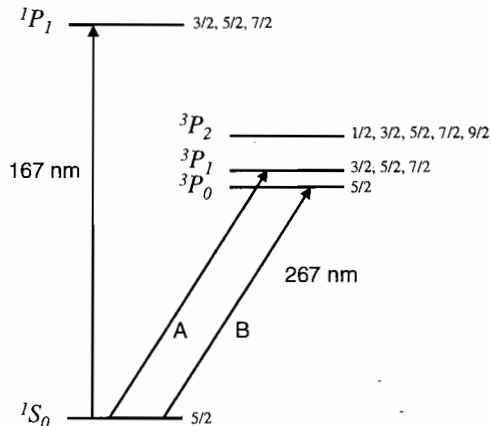


Fig. 2. The energy levels of $^{27}\text{Al}^+$ relevant to the operation of the frequency standard. The numbers to the right of the energy levels are the values of F , the total atomic angular momentum. The energy separations between hyperfine energy levels are not shown. The strong transition at 167 nm is not directly driven, for lack of a tunable laser at that wavelength. Transitions near 267 nm induced by the lasers are labeled A and B. The energy differences between the 3P_J fine-structure levels are expanded for clarity.

transition has a Q of 1.45×10^{17} , and is well suited as the basis for a frequency standard. However, there is no strongly-allowed transition that is available for laser cooling and fluorescence detection. The $3s3p$ 3P_1 state has a lifetime of 305 ± 10 μs ,²¹ and the $3s3p$ 3P_2 state has an even longer lifetime. The strongly-allowed 167 nm $3s^2$ 1S_0 to $3s3p$ 1P_1 transition would be useful for laser cooling and state detection, but narrowband, tunable lasers are not available at that wavelength. Since the nuclear spin of ^{27}Al has spin $I = 5/2$, both the 1S_0 and the 3P_0 state have total angular momentum $F = 5/2$. Therefore, each m_F sublevel of the 1S_0 and 3P_0 states has a linear Zeeman shift.

4.2. Operation of the Frequency Standard

To get around the cooling and detection problems, Wineland proposed to simultaneously trap an auxiliary ion, which could be

laser cooled and optically detected at a more convenient wavelength.²² Since the two ions are coupled through the Coulomb interaction, the $^{27}\text{Al}^+$ “clock” ion is also cooled. Further, the superposition state of the clock ion can be transferred to the auxiliary ion, making use of the fact that they share a vibrational degree of freedom. That is, if the state of the clock ion is $(\alpha|S\rangle + \beta|P\rangle)$, the state of the auxiliary ion becomes $(\alpha|1\rangle + \beta|2\rangle)$, where $|1\rangle$ and $|2\rangle$ are two of the hyperfine ground state sublevels. This makes it possible to detect whether the clock ion has been driven to the metastable state by observing the fluorescence of the auxiliary ion.

The basic methods were demonstrated at NIST with a $^{27}\text{Al}^+$ clock ion and a $^9\text{Be}^+$ auxiliary ion.²³ The $^{27}\text{Al}^+ 1S_0$ to 3P_1 transition (A in Fig. 2) was used for this demonstration. More recently, the $^{27}\text{Al}^+ 1S_0$ to 3P_0 transition (B in Fig. 2) has been observed.²⁰ This transition is the basis for the $^{27}\text{Al}^+$ optical frequency standard. Detection of the $1S_0$ to 3P_0 transition depends on the mapping of the $1S_0$ to 3P_1 superposition state to a superposition state of the $^9\text{Be}^+$ ion. Details of the methods used to frequency-lock a laser to the $^9\text{Be}^+ 1S_0$ to 3P_0 resonance have been published.²⁰

4.3. Limitations and Current Performance

The total fractional systematic uncertainty of the Al^+ clock frequency is 2.3×10^{-17} . The various contributions are discussed in detail elsewhere.^{17,20} The greatest part of the systematic uncertainty is due to the second-order Doppler shift, from both the thermal motion and the micromotion. The linear Zeeman shift is cancelled by observing Zeeman components with reversed m_F and averaging the frequencies. The blackbody radiation shift is unusually small for an optical frequency standard because of a fortuitous cancellation between the $1S_0$ and 3P_0 quadratic

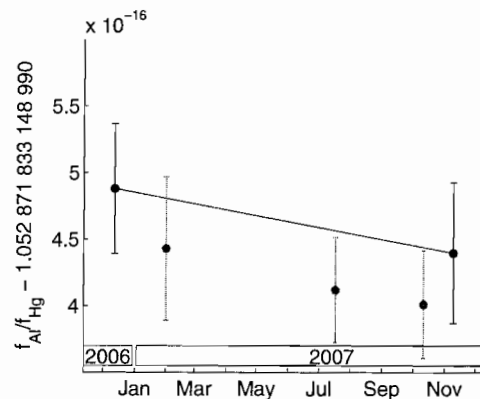


Fig. 3. Measurements of the ratio of the Al^+ and Hg^+ clock frequencies as a function of the date the measurements were made. The error bars are a combination of the statistical measurement uncertainties and the systematic uncertainties. The line connects the first point to the last one with a slope of $(-5.3 \pm 7.9) \times 10^{-17}/\text{year}$. The three points plotted in gray are not used in the calculation of the slope because not all of the systematic uncertainties were evaluated at the time of the measurements.

Stark shifts.²⁴ The fractional frequency shift at 300K is $(-8 \pm 5) \times 10^{-18}$. At the normal operating temperature of the frequency standard, it is $(-12 \pm 5) \times 10^{-18}$.

5. Hg^+ - Al^+ Frequency Comparisons

The Hg^+ and Al^+ frequency standards have been operated simultaneously. If one tooth of the femtosecond comb is phase-locked to one of the standards, and the heterodyne beat frequency between the other standard and the nearest tooth is measured, the frequency ratio of the two standards can be obtained in a way that does not depend on the accuracy of any microwave frequency standards used as references. The instability of the frequency ratio is described by an Allan deviation $\sigma_y(\tau)$ (fractional error for a measurement duration τ) of $3.9 \times 10^{-15} \tau^{-1/2}$ for $\tau > 100$, where τ is expressed in seconds.¹⁷ Both standards are thought to contribute approximately equally, in an uncorrelated man-

ner, to the instability of the ratio, so the fractional frequency instabilities of both standards are given by $\sigma_y(\tau) = 2.8 \times 10^{-15} \tau^{-1/2}$. Figure 3 is a plot of measurements of $f_{\text{Al}}/f_{\text{Hg}}$, the ratio of the frequency of the Al⁺ standard to that of the Hg⁺ standard. The reproducibility of the ratio is seen to be better than 1×10^{-16} , which is better than the accuracy of the primary Cs frequency standards. The weighted mean of the measurements of $f_{\text{Al}}/f_{\text{Hg}}$ is 1.052 871 833 148.990 438 (55), where the uncertainty is expressed in units of the least significant digit.¹⁷

6. Limits on Time Variation of Fundamental Constants

It is of interest to see whether the ratio $f_{\text{Al}}/f_{\text{Hg}}$ remains constant over time. If a systematic change in this quantity were observed, this might be due to a time variation of fundamental constants, such as the fine structure constant α , the strong interaction coupling constant α_s , or the ratios of the masses of elementary particles.²⁵ At present, no such change has been observed, which places stringent limits on variations of the fundamental constants. The slope of the fitted line in Fig. 3 corresponds to a fractional rate of change in α of $(1/\alpha)(d\alpha/dt) = (-1.6 \pm 2.3) \times 10^{-17}/\text{year}$, consistent with zero.

Acknowledgments

This work was supported by the Office of Naval Research, IARPA, and NIST. P. O. S. acknowledges support from the Alexander von Humboldt Foundation. This work was performed by an agency of the U. S. government and is not subject to U. S. copyright.

References

1. J. Terrien, *Metrologia* **4**, 41 (1968).
2. S. R. Jefferts *et al.*, *Proc. SPIE* **6673**, 667309 (2007).

3. S. A. Diddams, *et al.*, *Phys. Rev. Lett.* **84**, 5102 (2000).
4. D. J. Jones, *et al.*, *Science* **288**, 635 (2000).
5. R. Holzwarth, *et al.*, *Phys. Rev. Lett.* **85**, 2264 (2000).
6. B. C. Young, F. C. Cruz, W. M. Itano, and J. C. Bergquist, *Phys. Rev. Lett.* **82**, 3799 (1999).
7. R. H. Dicke, *Phys. Rev.* **89**, 472 (1953).
8. R. J. Rafac, *et al.*, *Phys. Rev. Lett.* **85**, 2462 (2000).
9. W. M. Itano, *et al.*, *Proc. SPIE* **6673**, 667303 (2007).
10. D. J. Berkeland and M. G. Boshier, *Phys. Rev. A* **65**, 033413 (2002).
11. S. A. Diddams, *et al.*, *Science* **293**, 825 (2001).
12. T. Udem, *et al.*, *Phys. Rev. Lett.* **86**, 4996 (2001).
13. S. Bize, *et al.*, *Phys. Rev. Lett.* **90**, 150802 (2003).
14. W. H. Oskay, *et al.*, *Phys. Rev. Lett.* **97**, 020801 (2006).
15. T. M. Fortier, *et al.*, *Phys. Rev. Lett.* **98**, 070801 (2007).
16. J. E. Stalnaker, *et al.*, *Appl. Phys. B* **89**, 167 (2007).
17. T. Rosenband, *et al.*, *Science* **319**, 1808 (2008).
18. D. J. Berkeland, *et al.*, *J. Appl. Phys.* **83**, 5025 (1998).
19. W. M. Itano, *J. Research National Institute of Standards and Technology* **105**, 829 (2000).
20. T. Rosenband, *et al.*, *Phys. Rev. Lett.* **98**, 220801 (2007).
21. E. Träbert, *et al.*, *J. Phys. B* **32**, 537 (1999).
22. D. J. Wineland, *et al.* in *Proceedings of the 6th Symposium on Frequency Standards and Metrology*, ed. P. Gill, (World Scientific, Singapore, 2002).
23. P. O. Schmidt, *et al.*, *Science* **309**, 749 (2005).
24. T. Rosenband, *et al.* in *Proc. 20th European Time and Frequency Forum* (2006); preprint: arXiv:physics/0611125v2.
25. S. N. Lea, *Rep. Prog. Phys.* **70**, 1473 (2007).